(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 0 829 328 A2

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
18.03.1998 Bulletin 1998/12

(51) Int. Cl.[6]: B24D 3/34, B24D 11/02, C09K 3/14

(21) Application number: 97120317.9

(22) Date of filing: 02.08.1993

(84) Designated Contracting States:
DE FR GB

(30) Priority: 19.08.1992 US 932161

(62) Document number(s) of the earlier application(s) in accordance with Art. 76 EPC:
93918581.5 / 0 656 031

(71) Applicant: Rodel, Inc.
Newark Delaware 19713 (US)

(72) Inventors:
- Reinhardt, Heinz F.
Chadds Ford, Pennsylvania 19317 (US)
- McClain, Harry George
Middletown, Delaware 19709 (US)
- Budinger, William D.
Newark, Delaware 19713 (US)
- Roberts, John V.H.
Newark, Delaware 19702 (US)
- Jensen, Elmer William
New Castle, Delaware 19720 (US)

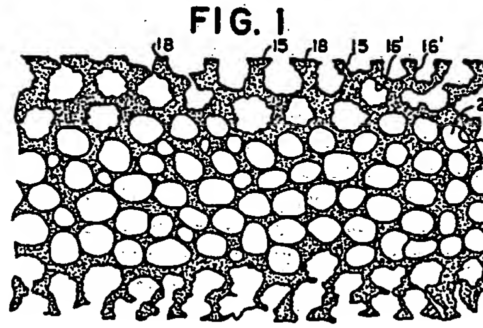
(74) Representative: Petersen, Frank
Lemcke, Brommer & Petersen,
Patentanwälte,
Bismarckstrasse 16
76133 Karlsruhe (DE)

Remarks:
This application was filed on 20.11.97 as a divisional application to the application mentioned under INID code 62.

(54) Polymeric substrate with polymeric microelements

(57) The present invention relates to a method of making or using an article of manufacture in the form of a polishing pad (10) for polishing or planarizing a surface of an electronic substrate, as well as a planarized semiconductor device made thereby. The pad comprises an elastomeric, polymeric matrix (14) impregnated with a plurality of hollow (22), flexible, polymeric microelements (16, 16'). The pad has a work surface (18) and a subsurface (24) proximate to the work surface. One portion (16') of the polymeric microelements is at the work surface and another portion (16) of the polymeric microelements is embedded within the subsurface of the pad that is not exposed to the working environment. The work surface of the pad is relatively softer than the subsurface as a result of mechanically opening or chemically altering the shells of at least some of the hollow, flexible, polymeric microelements located proximate the work surface such that the open polymeric microelements are less rigid than the polymeric microelements embedded in the subsurface, or by texturizing th work surface, thereby causing the work surface to be softer than the subsurface.

FIG. 1



Description

FIELD OF THE INVENTION

The invention relates to a polymeric substrate impregnated with polymeric microelements and methods of making and using the same and, more particularly, to an article of manufacture for use in polishing materials, such as semiconductor devices.

BACKGROUND OF THE INVENTION

Conventional polymeric substrates or polishing pads used for polishing, planarizing and other operations for which the present article is useful may be subjected to a variety of operating conditions which influence the selection of the substrate material. For example, variations in the nature of the workpiece being polished, polishing speed and pressure, elevated temperatures generated during the polishing operation, and the nature of any polishing slurry used in the operation may influence the choice of substrates.

Conventional polymeric polishing pads often vary in quality due to imprecise control of polymerization and blending processes and cutting and shaping of the final pad product. Therefore, the polishing characteristics imparted to a workpiece being polished, such as surface quality, stock removal rate and planarization rate, typically vary greatly between pad batches.

Conventional polishing pads are generally formed from multilayer laminations or stratified substrates having non-uniform physical properties throughout the thickness of the pad. An example of a typical stratified pad widely used for polishing semiconductor devices is the Politex Supreme pad, which is commercially available from Rodel, Incorporated, of Newark, Delaware. A typical Politex Supreme pad is composed of several layers, including a firm but resilient, 1 mm to 2 mm thick, porous bottom layer comprised of a polyester felt and polyurethane binder. A spongy and resilient microporous urethane layer of about 0.05 mm to 0.3 mm thickness is laminated onto the bottom layer. The top layer is comprised of vertical urethane structures having vertical, tapered pores, the taper of the pores narrowing toward the top of the pad. The top layer is very soft, porous and elastic. In a typical polishing operation, the top layer of such a stratified pad wears rapidly. As the top layer wears and subsequent layers are exposed, the polishing properties of the pad vary, resulting in non-uniform polishing rates and producing inconsistent polishing characteristics on the surface of the workpiece.

Conventional polishing pads typically have textured surfaces. The "microtexture" of a pad is the intrinsic icroscopic bulk texture of the pad after manufacture. Some of th factors which influence the static morphology or microscopic bulk texture of a conventional pad are the nature or texture of the work surface, such as waves, holes, creases, ridges, slits, depressions, protrusions ad gaps, and the size, shape, and distribution, frequency or spacing of individual features or artifacts. In typical polishing pads, the microtexture of the pad is largely random ad is the result of factors intrinsic to the manufacturing process. Because of the large number of variables in the manufacturing process, few attempts have been made to control variables such as pore size, shape and distribution. Other characteristics which may affect the pad texture are hardness, resilience, thickness, permeability, and resistivity, to name a few.

"Minitexturized" pads have intermediately sized textured artifacts on the pad, which may be produced by use of lasers or the incorporation of air or gas within the pad material.

"Macrotextures", or larger size textured artifacts, may be imposed on the work surface of a pad by embossing, skiving, perforating and/or machining, for example. In conventional polishing pads, the spacing and/or size of individual macrotexture artifacts or features is generally greater than 5 mm. The spacing and size of these artifacts are typically very regular and repetitive.

Conventional polishing pads may include various solid particulate such as cerium oxide, titanium oxide, aluminum oxide, barium carbonate, glass dust and fibers, diatomaceous earth, rouge, calcium carbonate, diamond, and carbon, for example. Typically, mechanical mixing and distribution of such particulates has been poorly controlled.

Japanese Patent Application No. JP-A-870224003, published on September 9, 1989, as Publication No. JP1071661, discloses a polishing pad for polishing a semiconductor wafer where the pad is a uniform polyurethane sheet including closed foam pores throughout the thickness of the sheet and a wavy surface. The surface of the pad is trued by the apparatus and process described in the application. The apparatus and process include using diamond pellets within a correction ring located between a center roller and a guide roller on a plate on which the pad is placed. In essence, the wavy surface of the pad is ground with the diamond pellets in a water slurry to flatten and thereby true the surface of the pad.

It would be desirable to have a substrate for polishing and other operations in which the particle distribution of additives may be optimized on a molecular scale. It is also desirable to have a polymeric substrate in which the surface of the substrate regenerates itself and does not vary appreciably as the surface is contacted with a workpiece. A polishing substrate which has a series of hardness variations on a micro scale and which can be texturized on a mini or macro scale to help remove dross (effluent, grindings, etc.) during polishing operations would also be advantageous.

SUMMARY OF THE INVENTION

Briefly, the present invention relates to methods of

making and using a article of manufacture in the form of a polishing pad for polishing or planarizing a surface of an electronic substrate, as well as a planarized semiconductor device that has been planarized using the pad.

The pad comprises an elastomeric, polymeric matrix impregnated with a plurality of hollow, flexible, polymeric microelements. The pad has a work surface and a subsurface proximate to the work surface. One portion of the polymeric microelements is at the work surface and another portion of the polymeric microelements is embedded within the subsurface of the pad that is not exposed to the working environment. The work surface of the pad is relatively softer than the subsurface as a result of the exposure of the one portion of the polymeric microelements to the working environment. The subsurface becomes the relatively softer work surface during wear of the pad when the polymeric microelements are exposed to the working environment.

One aspect of the present invention is a method for regenerating a work surface of the polishing pad. The method comprises the steps of: providing a pad as described above; and mechanically opening or chemically altering at least a portion of some of the shells of the hollow, flexible, polymeric microelements located proximate the work surface such that the open polymeric microelements are less rigid than the polymeric microelements embedded in the subsurface, thereby causing the work surface to be softer than the subsurface.

Another aspect of the present invention is a method for decreasing the effective rigidity of the work surface of a polishing pad as described above. The method comprises the steps of: providing a pad as described above; and texturizing the work surface including the hollow, flexible, polymeric microelements at the work surface, thereby causing the work surface to be less rigid than the subsurface.

A further aspect of the present invention is a method of planarizing a surface of a semiconductor device utilizing a planarizing pad as initially described in this Summary and contacting the surface of the semiconductor device in the presence of the working environment with the work surface of the pad.

An additional aspect of the present invention is a planarized semiconductor device that has been planarized using the pad described above.

BRIEF DESCRIPTION OF THE DRAWINGS

The foregoing summary, as well as the following detailed description of the preferred embodiments, will be better understood when read in conjunction with the appended drawings. For the purpose of illustrating the invention, there are shown in the drawings embodiments which are presently preferred, it being understood, however, that the invention is not limited to the specific methods and instrumentalities disclosed. In the drawings:

Fig. 1 is a schematic cross-sectional diagram of an article, in accordance with the present invention;
Fig. 2 is a schematic cross-sectional diagram of a alternative embodiment of an article according to the present invention;
Fig. 3 is a schematic cross-sectional diagram of an alternative embodiment of an article according to the present invention, in which microelements at the work surface of the article have swelled when in contact with the working environment;
Fig. 4 is a graph of planarization rate as a function of distance between features on the surface of a typical semiconductor device;
Fig. 5 is a schematic diagram of an alternative embodiment of a minitexturized pad according to the present invention;
Fig. 6 is an enlarged partial cross-sectional view of the pad of Fig. 5, taken along line 6-6;
Fig. 7 is a schematic diagram of an alternative embodiment of a macrotexturized pad according to the present invention;
Fig. 8 is an enlarged partial cross-sectional view of the pad of Fig. 7, taken along line 8-8;
Fig. 9 is a alternative embodiment of a fractal patterned minitexturized pad according to the present invention;
Fig. 10 is a bar graph showing specific gravity of a article according to the present invention as a function of the flow rate of microspheres; and
Fig. 11 is a schematic diagram of a device for pommelgating and puncturing a portion of shells of microelements at a work surface of a article according to the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Referring to the drawings, wherein like numerals indicate like elements throughout, there is shown in Figs. 1-3, 5-9 and 11 embodiments of a article of manufacture, generally designated 10, 110, 210, 310 and 410, in accordance with the present invention.

Preferably, the article 10 is a generally circular sheet or polishing pad 12, best shown in Figs. 5 and 7, although one of ordinary skill in the art would understand that the pad 12, may, for example, be generally square, rectangular or of any suitable shape, as desired.

The article 10 et seq. of the present invention may be used as a polishing pad either by itself or as a substrate in a polishing operation in which a polishing slurry is used to provide a desired surface finish for semiconductor devices, silicon devices, crystals, glass, ceramics, polymeric plastic material, metal, stone or other surfaces. Polishing pads 12 made with th articl 10 et

seq. of the present invention may be used with lubricants, coolants and various abrasive slurries, all well known to those skilled in the art and readily available commercially. Typical components of such slurries include liquid media, such as water or oil: abrasive agents, such as aluminum oxide, silicon carbide, silicon dioxide, cerium oxide and garnet; bases; acids; salts; surfactants, and/or other agents depending upon the nature of the workpiece. The working environment of the article comprises the environment surrounding the article when in use, including the substrate to be polished and the lubricants, coolants ad various abrasive slurries described above.

The article 10 et seq. is useful for altering a surface (not shown) of a workpiece (also not shown) by a polishing operation, such as planarizing or shaping. The workpieces to be polished preferably comprise friable substances, such as quartz, silicon, glass, electronic and optical substrates, and high density multi-component electronic devices, for example. The workpiece may be a semiconductor device (not shown) having multiple layers of polysilicone, thermal oxides, and metallic materials, each layer of which may be planarized before a subsequent layer is deposited thereon.

As best shown in Fig. 1, the article 10 comprises a polymeric matrix 14 which is preferably impervious to aqueous fluid slurries typically used in polishing and planarization operations. The polymeric matrix 14 may be formed from urethanes, melamines, polyesters, polysulfones, polyvinyl acetates, fluorinated hydrocarbons, and the like, and mixtures, copolymers and grafts thereof. One of ordinary skill in the art would understand that any other polymer having sufficient toughness and rigidity to resist abrasive wear during polishing operations may be used, in keeping with the spirit and scope of the present invention. As presently preferred, the polymeric matrix 14 comprises a urethane polymer. The urethane polymer is preferably formed from a polyether-based liquid urethane, such as the Adiprene line of products which are commercially available from Uniroyal Chemical Co., Inc. of Middlebury, Connecticut. The preferred liquid urethane contains about 9 to about 9.3% by weight free isocyanate. Other isocyanate bearing products and prepolymers may also be used in keeping with the spirit and scope of the present invention.

The liquid urethane is preferably one which reacts with a polyfunctional amine, diamine, triamine or polyfunctional hydroxyl compound or mixed functionality compounds such as hydroxyl/amines dwelling in urethane/urea crosslinked networks to permit the formation of urea links and a cured/crosslinked polymer network. As presently preferred, the liquid urethane is reacted with 4,4'-methylene-bis [2-chloroaniline] ("MOCA"), which is commercially available as the product Curene® 442, from Anderson Development Co. of Adrian, Michigan.

As best shown in Fig. 1, the polymer matrix 14 is impregnated with a plurality of polymeric microelements 16. Preferably, at least a portion of the polymeric microelements are generally flexible. Suitable polymeric microelements include sugars and water-soluble gums and resins. Examples of such polymeric microelements include polyvinyl alcohols, pectin, polyvinyl pyrrolidone, hydroxyethylcellulose, methylcellulose, hydropropylmethylcellulose, carboxymethylcellulose, hydroxypropylcellulose, polyacrylic acids, polyacrylamides, polyethylene glycols, polyhydroxyetheracrylites, starches, maleic acid copolymers, polyethylene oxide, polyurethanes and combinations thereof. The microelements 16 may be chemically modified to change the solubility, swelling and other properties by branching, blocking, and crosslinking, for example.

As presently preferred, each of the polymeric microelements 16 has a mean diameter which is less than about 150 μm, and more preferably a mean diameter of about 10 μm. One of ordinary skill in the art would understand that the mean diameter of the microelements may be varied and that microelements 16 of the same or different sizes or mixtures of different microelements 16 may be impregnated in the polymeric matrix 14, as desired.

As presently preferred, each of the polymeric microelements 16 are spaced apart about 1 μm to about 100 μm. Preferably, the polymeric microelements 16 are substantially uniformly distributed throughout the polymeric matrix 14 by high shear mixing. The resulting composite mixture is transferred to a conventional mold before the viscosity of the reacted urethane polymer becomes too great to permit sufficient blending of the microelements with the polymer mixture. One of ordinary skill in the art would understand that the low viscosity window may vary at different temperatures for different thermosetting plastics and curing agents. The resulting mixture is gelled in the mold for about 15 minutes. The gelling time may vary based upon factors such as temperature and selection of the polymer matrix and microelements. The composite is then cured at about 200-225°F for about 4-6 hours and cooled to room temperature (about 70°). The curing temperature may vary depending upon the polymer matrix and type of microelements used, among other factors.

The resulting article 10 is removed from the mold and cut, sliced etc. to the desired thickness and shaped to form polishing pads 12. One of ordinary skill in the art would understand that the molded composite may be sliced, cut or otherwise machined to any thickness or shape as desired, in accordance with the present invention.

Depending upon the intended application or operation, at least a portion of the polymeric microelements 16 may be generally spherical in shape, as shown in Fig. 1. Preferably such microspheres are hollow, each microsphere having a shell with a thickness of about 0.1 μm.

As best shown in Fig. 1, each polymeric microelement 16 has a void space 22 therein. At least some of the polymeric microelements 16 preferably have a plurality of void spaces 22 therein, as best shown in Fig. 3. It is preferred (but not required) that each void space 22 generally contains a gas at a pressure greater than atmospheric pressure to help maintain the structural integrity of the microelements 16',16, respectively, both at the work surface 18 and subsurface 24 of the polymeric matrix 14.

The polymeric microelements may have permeable or puncturable shells 20, best shown in Fig. 11, so that the void spaces 22 within the microelements 16' may be rendered open to the working environment.

As best shown in Fig. 1, in a preferred embodiment of the present invention, at least a portion of the polymeric microelements 16' located at the work surface 18 soften upon contact with the working environment (not shown) or polishing slurry. For example, water soluble cellulose ethers such as methylcellulose will dissolve upon contact with water in an aqueous polishing slurry.

As best shown in Fig. 1, in another preferred embodiment, at least a portion of the polymeric microelements 16' located at the work surface 18 swell upon contact with the working environment. For example, longer chain cellulose ethers may swell upon contact with water in an aqueous polishing slurry.

The article 10 has a work surface 18 and a subsurface 24 proximate to the work surface 18, as best shown in Figs. 1-3. Preferably, the work surface 18 is about 5 µm to about 60 µm thick. The thickness of the article 10 is preferably between about 300 µm and about 400 µm in a direction generally perpendicular to a major plane (not shown) of the work surface 18.

An advantage of the present invention is that polymeric microelements 16' at the work surface 18 of the article 10 are less rigid than the polymeric microelements 16 embedded in the subsurface 24 when the article 10 is in contact with the working environment. Also, the less rigid polymeric microelements 16' provide less support for the portion 15 of the polymeric matrix 14 which surrounds the less rigid microelements, thereby reducing the effective rigidity of that surrounding portion 15 of the polymeric matrix. Therefore, at least two levels of hardness are created in the article 10, the work surface 18 being generally softer than the subsurface 24.

Another advantage of the present invention is that as the work surface 18 of the article wears, such as by contact with the surface of a workpiece or the working environment, the subsurface 24 immediately adjacent to the work surface 18 becomes the new work surface and the two levels of hardness are regenerated continuously, which permits more even and consistent polishing of the workpiece and more even wear of the pad 12.

Different aspects of the present invention will now be described and explained further by reference to the following specific, illustrative, non-limiting examples.

Example 1

A polymeric matrix was prepared by mixing 2997 grams of Uniroyal Adiprene L-325 polyether-based liquid urethane with 768 grams of Curene® 442 (4,4'-methylene-bis [2-choloroaniline] ("MOCA") at about 150°F. At this temperature, the urethane/polyfunctional amine mixture has a pot life of about 2.5 minutes (the "low viscosity window").

During this low viscosity window, 69 grams of Expancel 551 DE hollow polymeric microspheres were blended with the polymer mixture at 3450 rpm using Rodel Incorporated high shear blending and mixing equipment to generally evenly distribute the microspheres in the polymer mixture. The mixture was transferred to a conventional mold during the low viscosity window and permitted to gel for about 15 minutes.

The mold was next placed in a curing oven, such as is commercially available from Koch Oven Corporation. The mixture was cured in the oven for about 5 hours at about 200°F. The power to the oven was then shut off and the mixture permitted to cool in the oven for about 4-6 hours until the temperature of the molded article 10 was about 70°F (room temperature). The molded article was then cut to form polishing pads. The mean distance between the microspheres in the resulting polishing pad 12 is believed to be between about 75 and about 300 µm.

As shown in Fig. 4, the planarization rate (μm^{-1}) is more than four times greater for a 20 mil thick urethane pad having Expancel microspheres embedded therein (as designated by the squares) than a similar urethane pad without microspheres (as designated by the circles) when the pads were used to planarize a typical semiconductor device having features or chips spaced about 1 mm apart. In other words, Fig. 4 shows that a device may be planarized about four times faster by using a urethane pad having microelements embedded therein than without microelements, according to the present invention.

As shown in Fig. 10, the specific gravity of the molded article decreases as the flow rate of microspheres is increased. Generally, it is preferred that the specific gravity of the pad be about 0.75 to about 0.8, which corresponds to an Expancel microsphere flow rate of about 53 grams/minute.

In alternative embodiments best shown in Figs. 5-9, the work surface 18 of the article 10 may further include a mini or macro pattern or texture 26 which includes recessed and/or elevated portions or artifacts 28. The texture 26 may be formed upon at least a portion of the work surface 18 by mechanical texturizing methods, such as machining, embossing, turning, grinding, replicating and lasering the work surface 18. One of ordinary skill in th art would understand that the texture 26 may be formed by a variety of other mechanical work or chemical methods, such as etching, for example.

By texturizing the work surfac 18, up to 50% or

more surface area may be exposed to facilitate removal of dross during polishing. In addition, texturing of the work surfac 18 enhances the polishing action by exposing a greater number of microelements 16' to the working environment. The texture 26 may be formed in a variety of patterns, contours, grooves, spirals, radials, dots, or any other shape as desired. Texturing the work surface 18 of the pad 12 offers a series of hardness variations on the microscale. For example, the artifacts 28 may be shaped to form cones or blades having a harder core and a softer outer surface in addition to the harder subsurface 24.

Preferably, the artifacts 28 are spaced apart between about 0.1 mm to about 10 mm and have a depth between about 1 mm and about 10 mm. Generally, it is preferred that the artifacts 28 have a length in a first dimension less than about 1000 times a mean diameter of a polymeric microelement 16. It is also preferred that the artifacts 28 have a depth less about 2000 times a mean diameter of a polymeric microelement 16.

As best shown in Figs. 5 and 6, the work surface 18 may include a minitexture including artifacts 28 having a width between about 1000 µm and 5 mm. The minitexture shown in Figs. 5 and 6 is a concentric circular pattern, although one of ordinary skill in the art would understand that the minitexture may be a spiral or other pattern, including those discussed above.

As best shown in Figs. 7 and 8, the work surface 18 may include a macrotexture including artifacts 28, each artifact 28 having a width greater than about 5 mm. As shown in Figs. 7 and 8, the minitexture is a generally square grid, although one of ordinary skill in the art would understand that the minitexture may be formed in any pattern, including those discussed above, as desired.

The macrotexture and minitexture may be formed by typical machining methods, such as embossing, turning, grinding, replicating and lasering and a variety of other methods well known to those of ordinary skill in the art.

Example 2

Using a standard lathe and a single point tool, the work surfaces 18 shown in Figs. 5-8 were cut by superimposing circular and square grid patterns, respectively, on the work surface 18 which was vacuum mounted to the lathe or milling machine's rotating plate. A conventional horizontal milling machine with ganged cutting tools or custom cutting combs with regularly spaced serrated teeth was used to machine the work surface 18 in the desired pattern.

As best shown in Fig. 5, the annular minitexture was machined into the polishing pad to form grooves having 1.397 mm (0.055") pitch, each with a depth of 0.356 mm (0.014"). The groove form is buttress thread with a 60 degree ramp towards the pad's inside diameter, as shown in Fig. 6.

The square grid macrotexture 28 shown in Figs. 7 and 8 was machined on a horizontal milling machine to produce squares having grooves 0.8013 mm (0.032") wide and 0.635 mm (0.025") deep defining 6.35 mm (0.25") artifacts 28.

As best shown in Fig. 9, the work surface 18 may also include a minitexture including artifacts 28 having a width between about 1000 µm and 5 mm produced by use of a carbon dioxide laser. Preferably, the microtexture is produced in the shape of a fractal pattern on the work surface 18. As herein defined "fractal patterned means a repeating pattern which has repeating artifacts in which the artifacts are different from each other. The fractal pattern may be generated by deterministic or non-deterministic mathematical formulas, such as the Gosper Island variant of the Koch Island & Lake fractal pattern ("Gosper pattern") (shown in Fig. 9). Suitable fractal models include the round, spherical and swiss-cheese tremas, although one of ordinary skill in the art would understand that other suitable fractal patterns may be used in accordance with the present invention, as desired. Preferably, the fractal pattern is chaotic or random.

Example 3

As best shown in Fig. 9, grooves or minitextures were machined into a polishing pad 12 using a typical carbon dioxide laser with a continuous wave output of 100 watts. The power rating, output and beam focus were selected to cut a groove with a depth of about 0.458 mm (0.018") and having a width of less than about 0.127 mm (0.005"). The minitexture was the Gosper Island variation of the Koch Island & Lake fractal pattern discussed above. The fractal pattern image was read and programmed electronically into a conventional computer numerical controller, which controlled movement of the laser beam to form the fractal pattern on the work surface 18 of the pad 12. An adhesive mask was used to eliminate vapor trails from accumulating on the pad. The adhesive mask also reduced the attendant minor fusing on the edges of the grooves.

Alternatively, or additionally, isolated "mesa" patterns may be embossed onto the work surface 18 to form a minitexture. For example, a conventional 30 ton press machine may be used to apply about 25 tons of pressure to emboss a minitexture onto the work surface 18 of a pad 12. Heat may be applied to enhance the embossing effect.

The method according to the present invention of planarizing a surface of a semiconductor device utilizing an article 10 *et seq.* according to the present invention will now be described generally.

With reference to Figs. 1-3, the method generally comprises the initial step of providing an article 10 or 110 comprising a polymeric matrix 14. The polymeric matrix 14 is impregnated with a plurality of polymeric microelements 16. The details of providing the poly-

meric matrix 14 and impregnating the matrix 14 with the microelements 16 are discussed above and further discussion thereof is not believed to be necessary nor is it limiting. Preferably, the work surfac 18 of the article 10 or 110 is textured to form artifacts 28 to provide an enlarged work surface area and expose microelements 16 to the working environment which would not normally be exposed if the work surface 18 were generally flat.

The method further comprises the step of contacting at least a portion of the work surface 18 of the article 10 or 110 with the working environment such that the polymeric microelements 16' at the work surface 18 of the article 10 or 110 are less rigid than the polymeric microelements 16 located in the adjacent subsurface 24. For example, a portion of a shell 20 of at a portion of the polymeric microelements 16 located proximate the work surface 18 may be opened by at least one of skiving, abrading, cutting and puncturing a portion of the shell 20 or by chemically altering or softening a portion of the shell 20 to render a portion of the polymeric microelements 16' of the work surface 18 less rigid than the microelements 16 located in the subsurface 24. Details as to how the polymeric microelements 16' at the work surface 18 may be made less rigid are discussed above and further discussion thereof is not believed to be necessary nor limiting.

The method further comprises the step of contacting the surface (not shown) of the semiconductor device (also not shown) with at least a portion of the work surface 18 of the article such that the surface of the semiconductor device is sufficiently planarized. The article 10 or polishing pad 12 may be attached to a conventional polishing machine such as are well known to those of ordinary skill in the art. Preferably, the work surface 18 is oriented generally parallel to the surface of the semiconductor device to be planarized and may be moved in linear or circular sliding contact, for example, to planarize or abrade the surface of the semiconductor device, as desired.

As the work surface 18 of the pad 12 is abraded by sliding contact with the surface of the semiconductor device, portions of the subsurface 24 are exposed and microelements 16 in the subsurface 24 are abraded or chemically altered or softened to form a new work surface 18 having similar physical properties to the previously abraded work surface. Therefore, the work surface 18 in contact with the surface of the semiconductor device is essentially continuously regenerated to provide a consistent planarizing or polishing action upon the surface of the semiconductor device.

A method according to the present invention of regenerating the work surface 18 of an article according to the present invention will now be described generally.

Referring now to Fig. 11, the method generally comprises the initial steps of providing an article 410 or pad 12 comprising a polymeric matrix 14 and impregnating the matrix 14 with a plurality of polymeric microelements 16. The details of forming the articl 10 are discussed at length above and further discussion thereof is not believed to be necessary nor limiting.

The method further comprises the step of opening at least a portion of a shell 20 of at least a portion of the polymeric microelements 16 located proximate to the work surface 18 such that the open microelements 16' are less rigid than the microelements 16 in the subsurface 24. The step of opening the polymeric microelements may include at least one of skiving, abrading, cutting and puncturing a portion of each of the shells 20 of the microelements 16. As best shown in Fig. 11, the shells 20 of the microelements 16' at the work surface 18 may be punctured by a combined pommelgation and perforation device 30, a portion of which is shown in cross-section in Fig. 11. The device 30 may be formed from any material having sufficient rigidity to puncture the work surface 18 and microelements 16, such as stainless steel, aluminum and other metals, for example. The device 30 includes a plurality of sharp implements or needles 32 for puncturing at least a portion of a shells 20 of polymeric microelements 16 located proximate the work surface 18.

In addition to the needles 32, the device 30 includes at least one, and preferably a plurality of pads 34 for preventing the needles 23 from puncturing the work surface 18 too deeply. Preferably, the needles 32 puncture the work surface 18 to a depth of about 60 µm, although one of ordinary skill in the art would understand that the puncturing depth of the device 30 may any depth greater or less than 60 µm, as desired. For example, longer needles 32 could be used to puncture the work surface 18 to a depth greater than 60 µm.

One of ordinary skill in the art would understand that the microelements 16 may be opened or the pad 12 may be punctured one or more times, as needed.

In an alternative embodiment, at least a portion of the shells 20 of polymeric microelements 16 located proximate the work surface 18 may be chemically altered or softened by the work environment such that the partially altered polymeric microelements 16 at the work surface 18 are less rigid than the polymeric microelements 16 embedded in the subsurface 24. For example, the polymeric microelements 16 may be formed from water soluble cellulose ethers comprising methylcellulose or hydroxypropylmethylcellulose which at least partially dissolve when contacted with a working environment comprising water.

From the foregoing description, it can be seen that the present invention comprises articles of manufacture for altering a surface of a workpiece, such as a semiconductor device, and methods for decreasing the effective rigidity of a polymeric microelement located at a portion of a work surface of such an article, regenerating the work surface of such an article, and planarizing a surface of a semiconductor device utilizing such an article. The present articles may be used to more rapidly and evenly polish or planarize a substrate or other workpiece.

It will be appreciated by those skilled in the art that other changes could be made to the embodiments described above without departing from the broad inventiv concept thereof. It should be understood, therefore, that this invention is not limited to the particular embodiments disclosed, but it is intended to cover all modifications which are within the spirit and scope of the inventions as defined by the appended claims.

Claims

1. A method for regenerating a work surface of a polishing pad for polishing or planarizing a surface of an electronic substrate, the method comprising the steps of:

   providing a polishing pad (10, 12, 110, 210, 310, 410) comprising an elastomeric, polymeric matrix (14) impregnated with a plurality of hollow, flexible, polymeric microelements (16), the pad having a work surface (18) and a subsurface (24) proximate to the work surface, one portion (16') of the polymeric microelements being at the work surface and exposed to a working environment including a polishing slurry, another portion of the polymeric microelements (16) being embedded within the subsurface (24) of the pad that is not exposed to the working environment; and
   mechanically opening or chemically altering at least a portion of some of the shells of the hollow, flexible, polymeric microelements located proximate the work surface such that the open polymeric microelements are less rigid than the polymeric microelements embedded in the subsurface, thereby causing the work surface to be softer than the subsurface.

2. A method for decreasing the effective rigidity of a polishing pad work surface, the method comprising the steps of:

   providing a polishing pad (10, 12, 110, 210, 310, 410) comprising an elastomeric, polymeric matrix (14) impregnated with a plurality of hollow, flexible, polymeric microelements (16), the pad having a work surface (18) and a subsurface (24) proximate to the work surface, one portion (16') of the polymeric microelements being at the work surface and exposed to a working environment including a polishing slurry, another portion of the polymeric microelements (16) being embedded within the subsurface (24) of the pad that is not exposed to the working environment; and
   texturizing the work surface including the hollow, flexible, polymeric microelements at the work surface, thereby causing the work surface to be less rigid than the subsurface.

3. A method of planarizing a surface of a semiconductor device with a polishing pad, the method comprising the steps of:

   providing a polishing pad (10, 12, 110, 210, 310, 410) comprising an elastomeric, polymeric matrix (14) impregnated with a plurality of hollow, flexible, polymeric microelements (16), the pad having a work surface (18) and a subsurface (24) proximate to the work surface, one portion (16') of the polymeric microelements being at the work surface and exposed to a working environment including a polishing slurry, another portion of the polymeric microelements (16) being embedded within the subsurface (24) of the pad that is not exposed to the working environment; and
   contacting the surface of the semiconductor device in the presence of the working environment with the work surface of the pad.

4. A method according to claim 1, 2 or 3, wherein the polymeric microelements are substantially uniformly distributed throughout the polymeric matrix.

5. A method according to claim 1, 2 or 3, wherein the polymeric matrix comprises a urethane polymer.

6. A method according to claim 1, 2 or 3, wherein at least a portion of the polymeric microelements located at the work surface soften upon exposure to the working environment.

7. A method according to claim 1, 2 or 3, wherein at least a portion of the polymeric microelements located at the work surface swell upon exposure to the working environment.

8. A method according to claim 1, 2 or 3, wherein at least some of the polymeric microelements contain a plurality of void spaces (22) therein.

9. A method according to claim 1, 2 or 3, wherein the hollow polymeric microelements contain a gas at a pressure greater than atmospheric pressure.

10. A method according to claim 1, 2 or 3, wherein each of the polymeric microelements has a mean diameter less than about 150 μm.

11. A method according to claim 10, wherein said mean diameter of each of the polymeric microelements is about 10 μm.

12. A method according to claim 1, 2 or 3, wherein the polymeric microelements are spaced apart by

about 1 μm to about 100 μm.

13. A method according to claim 1, 2 or 3, wherein at least some of th polymeric microelements are generally spherical in shape.

14. A method according to claim 1, 2 or 3, wherein at least some of the polymeric microelements have permeable shells so that the hollow microelements may be rendered open to the working environment.

15. A method according to claim 1, 2 or 3, wherein the work surface is about 5 μm to about 60 μm thick.

16. A method according to claim 2, wherein the work surface comprises a microtexture (26) integral with the pad, the microtexture including an artifact (28) having a width less than about 1000 μm.

17. A method according to claim 2, wherein the work surface comprises a minitexture (26) integral with the pad, the minitexture including an artifact (28) having a width of about 1000 μm to about 5 mm.

18. A method according to claim 2, wherein the work surface comprises a macrotexture (26) integral with the pad, the macrotexture including an artifact (28) having a width greater than about 5 mm.

19. A method according to claim 2, wherein the work surface comprises a texture (26) integral with the pad, the texture including a plurality of artifacts (28), each of the artifacts being spaced apart of about 0.1 mm to about 10 mm and having a depth of about 1 mm to about 10 mm.

20. A method according to claim 2, wherein the work surface comprises a texture (26) integral with the pad, the texture including an artifact (28) having a length less than about 1000 times a mean diameter of the polymeric microelements.

21. A method according to claim 2, wherein the work surface further comprises a texture (26) integral with the pad, the texture including an artifact (28) having a depth less than about 2000 times a mean diameter of polymeric microelements.

22. A planarized semiconductor device made by planarizing a surface of the semiconductor device in the presence of the working environment by a pad in accordance with the method of any one of claims 3 through 21.

FIG. 1

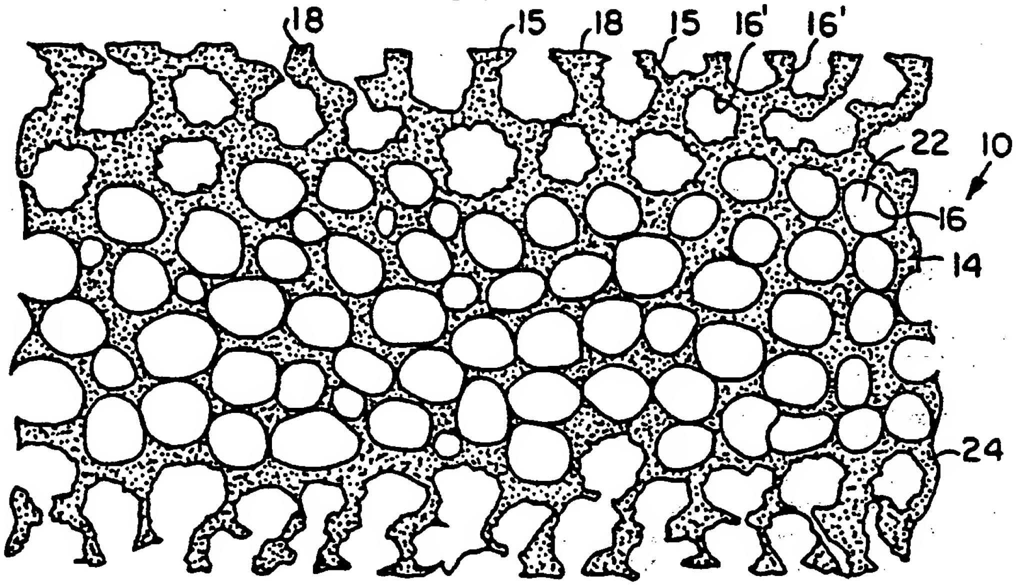


FIG. 2

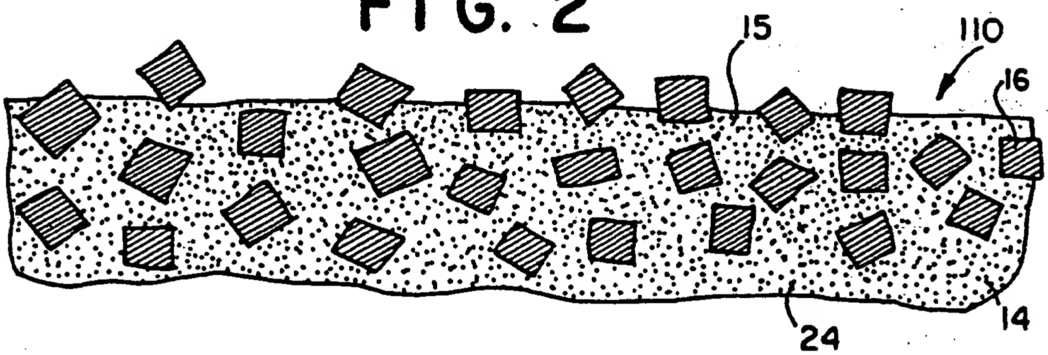


FIG. 3

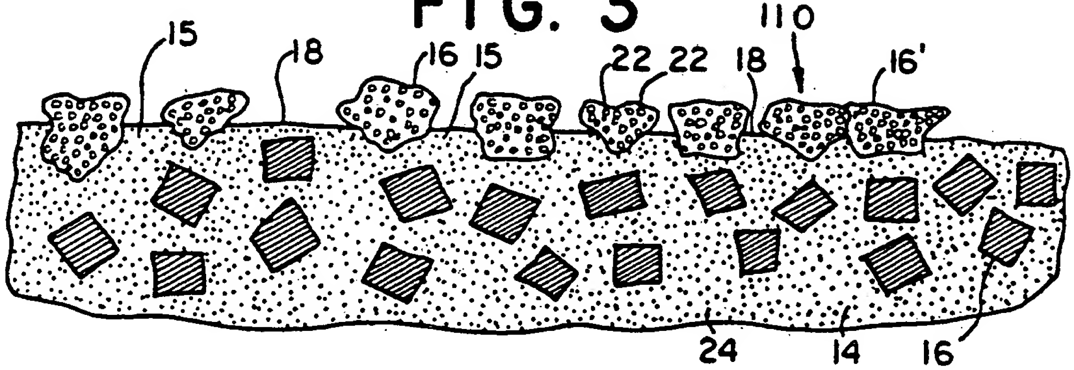
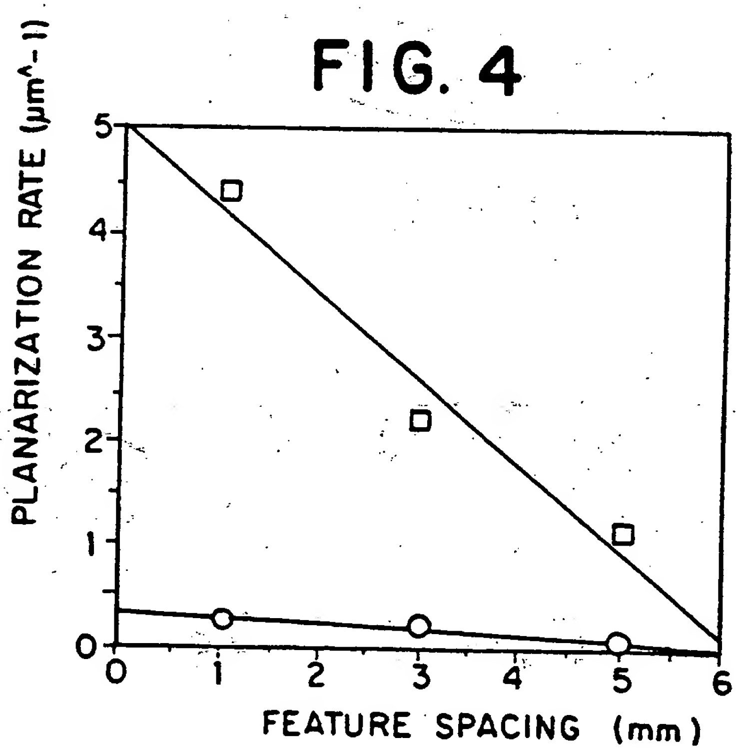

15
18
16
15
22
22
18
110
16'
24
14
16

FIG. 4


PLANARIZATION RATE (µm^-1)
0
1
2
3
4
5
0
1
2
3
4
5
6
FEATURE SPACING (mm)

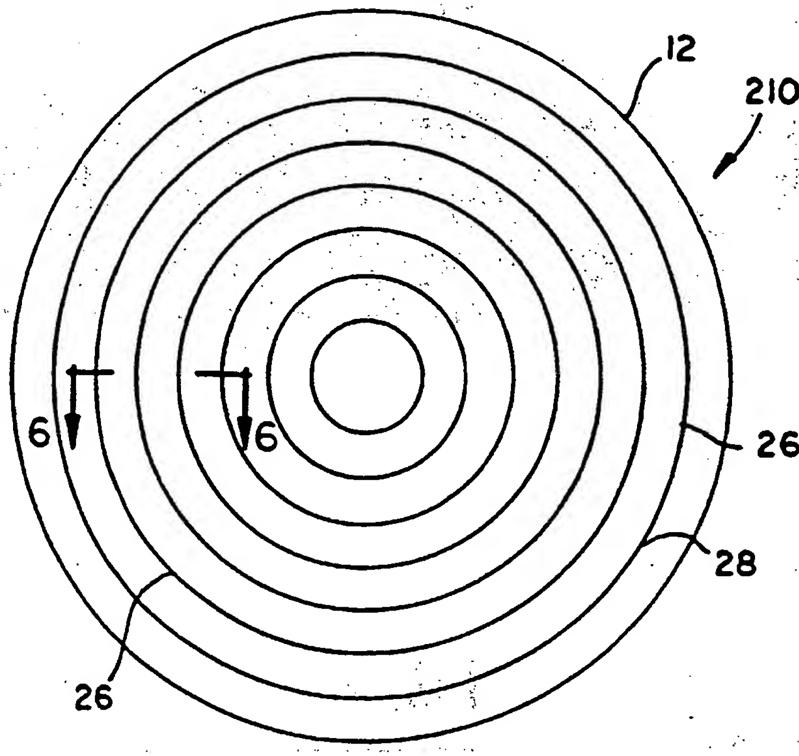


FIG. 5

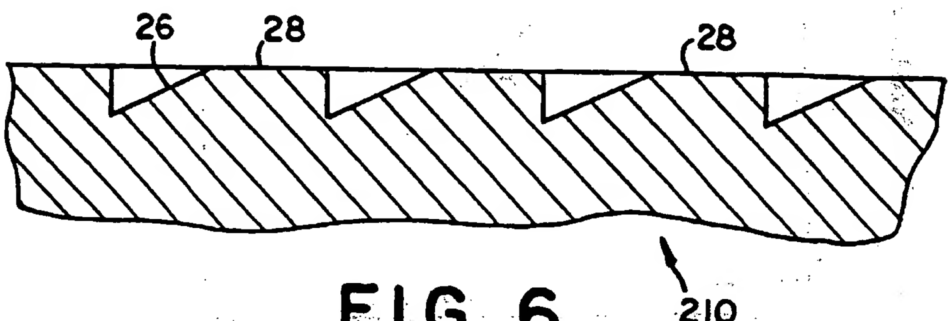


FIG. 6

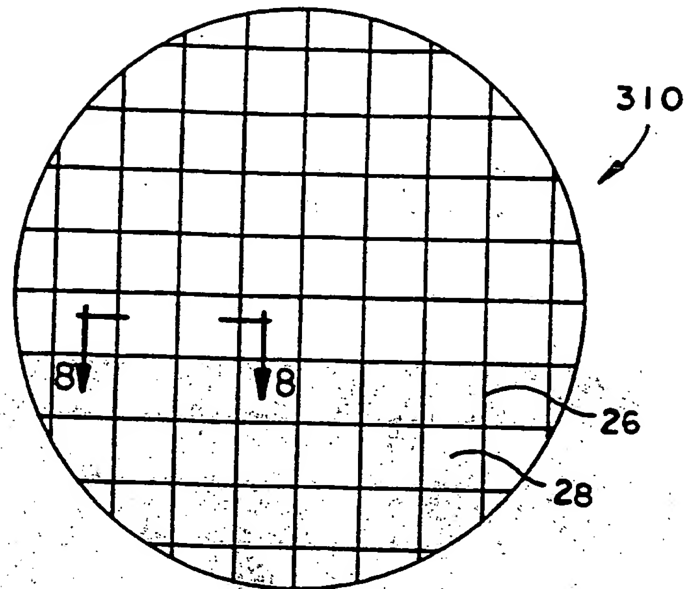


FIG. 7

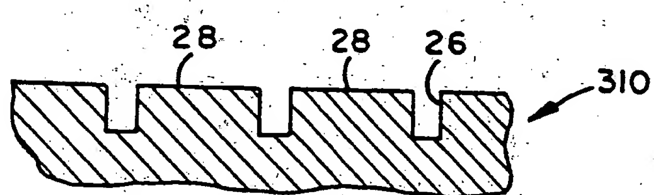


FIG. 8

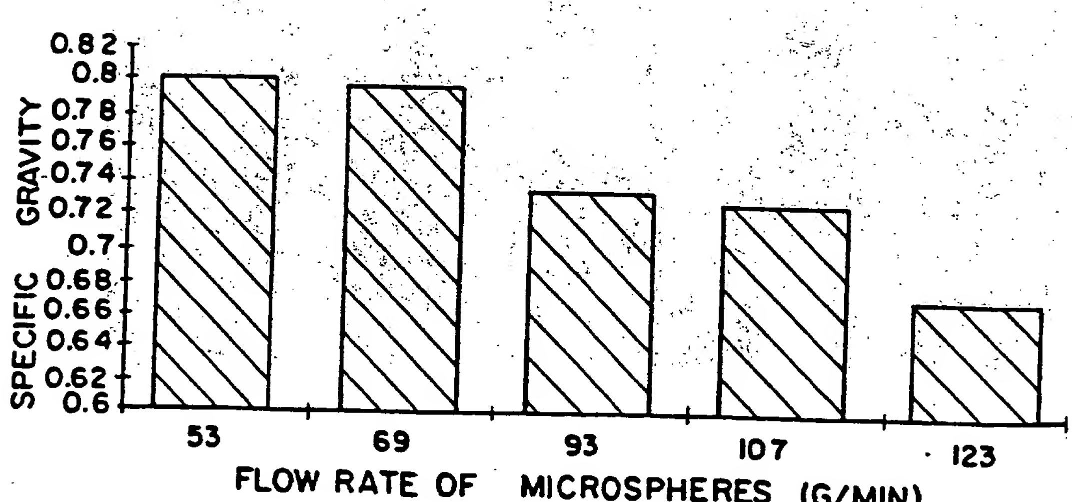
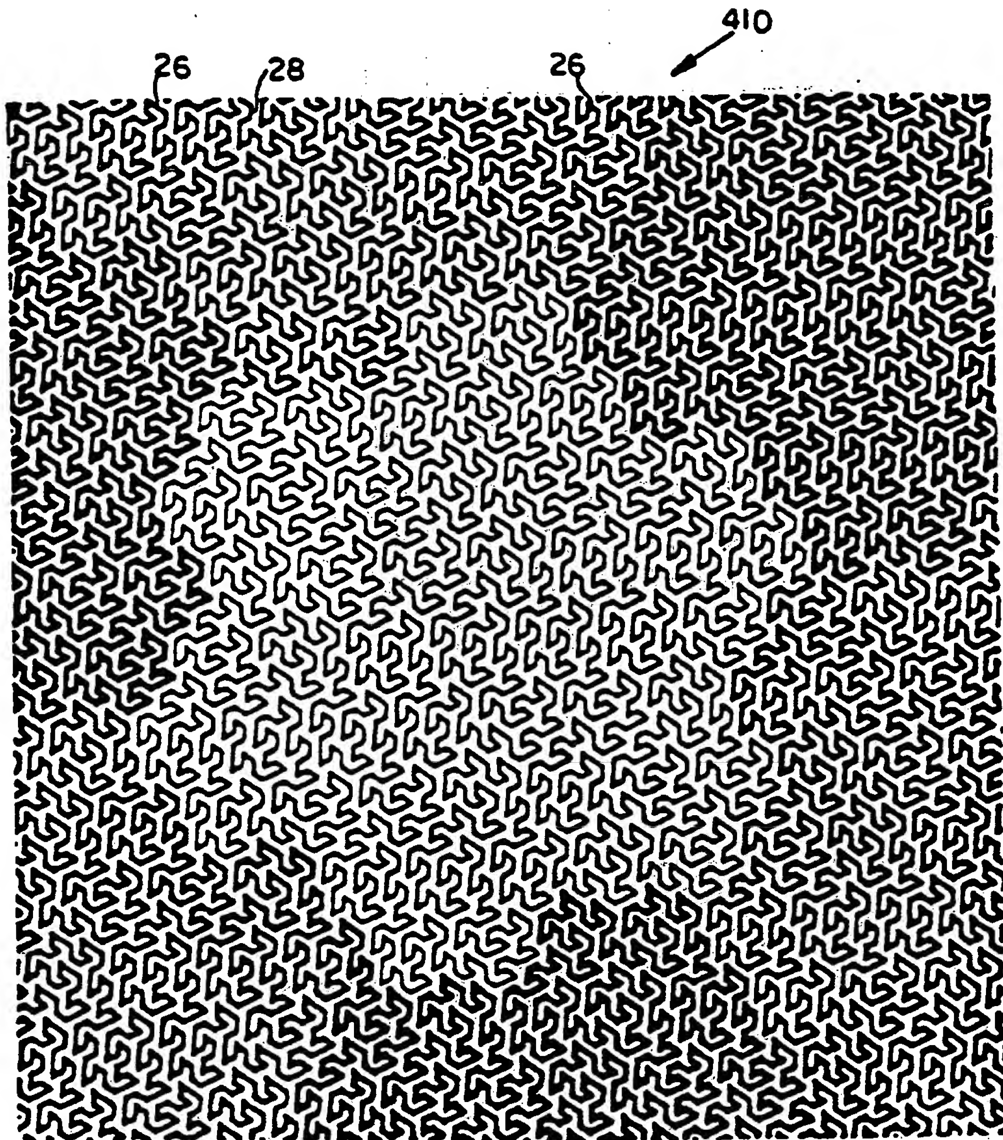


FIG. 10

FIG. 9



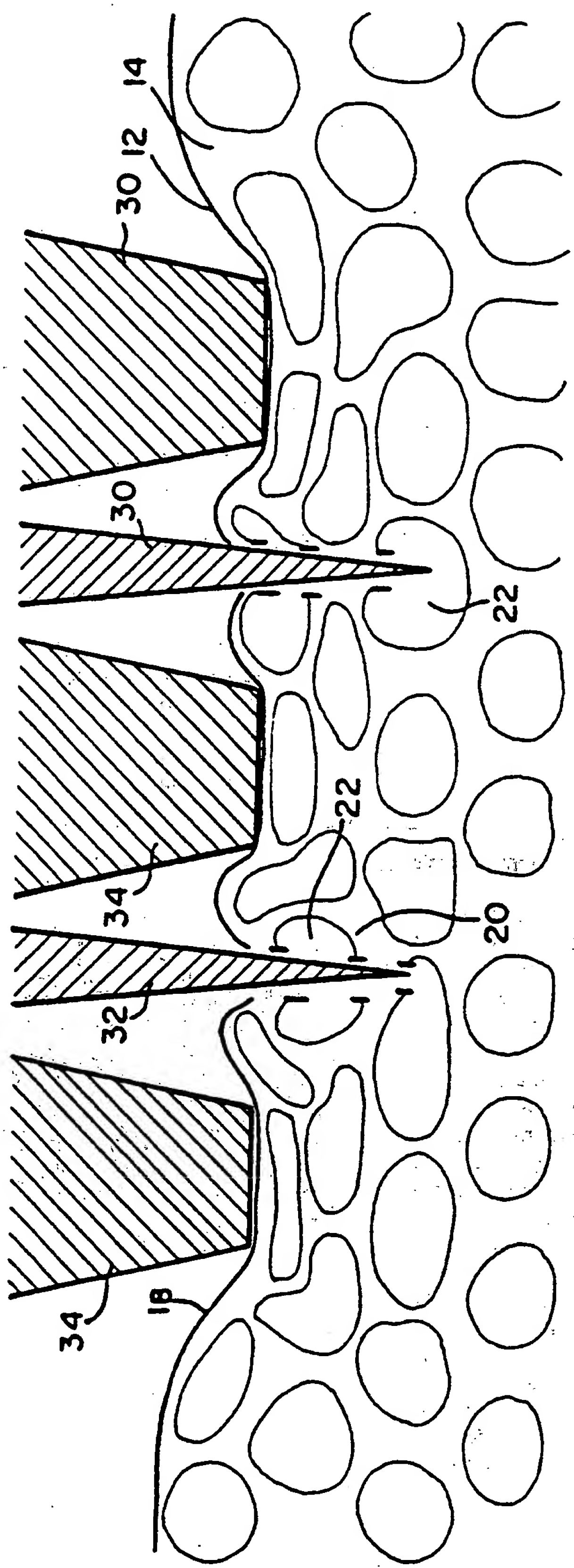


FIG. 11

(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 0 829 328 A3

(12) **EUROPEAN PATENT APPLICATION**

(88) Date of publication A3:
09.12.1998 Bulletin 1998/50

(51) Int. Cl.[6]: **B24D 3/34**, B24D 11/02, C09K 3/14

(43) Date of publication A2:
18.03.1998 Bulletin 1998/12

(21) Application number: **97120317.9**

(22) Date of filing: **02.08.1993**

(84) Designated Contracting States:
DE FR GB

(30) Priority: **19.08.1992 US 932161**

(62) Document number(s) of the earlier application(s) in accordance with Art. 76 EPC:
93918581.5 / 0 656 031

(71) Applicant: **Rodel, Inc.**
Newark Delaware 19713 (US)

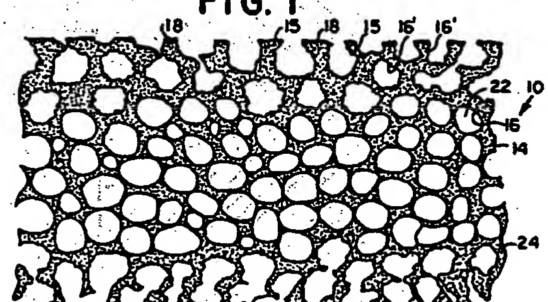
(72) Inventors:
- **Reinhardt, Heinz F.**
  Chadds Ford, Pennsylvania 19317 (US)
- **McClain, Harry George**
  Middletown, Delaware 19709 (US)
- **Budinger, William D.**
  Newark, Delaware 19713 (US)
- **Roberts, John V.H.**
  Newark, Delaware 19702 (US)
- **Jensen, Elmer William**
  New Castle, Delaware 19720 (US)

(74) Representative:
Petersen, Frank, Dipl.-Ing.
Lemcke, Brommer & Partner
Patentanwälte
Bismarckstrasse 16
76133 Karlsruhe (DE)

(54) **Polymeric substrate with polymeric microelements**

(57) The present invention relates to a method of making or using an article of manufacture in the form of a polishing pad (10) for polishing or planarizing a surface of an electronic substrate, as well as a planarized semiconductor device made thereby. The pad comprises an elastomeric, polymeric matrix (14) impregnated with a plurality of hollow (22), flexible, polymeric microelements (16, 16'). The pad has a work surface (18) and a subsurface (24) proximate to the work surface. One portion (16') of the polymeric microelements is at the work surface and another portion (16) of the polymeric microelements is embedded within the subsurface of the pad that is not exposed to the working environment. The work surface of the pad is relatively softer than the subsurface as a result of mechanically opening or chemically altering the shells of at least some of the hollow, flexible, polymeric microelements located proximate the work surface such that the open polymeric microelements are less rigid than the polymeric microelements embedded in the subsurface, or by texturizing the work surface, thereby causing the work surface to be softer than th subsurface.

FIG. 1



EP 0 829 328 A3

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 97 12 0317

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	PATENT ABSTRACTS OF JAPAN vol. 013, no. 274 (M-841), 23 June 1989 & JP 01 071661 A (SHOWA DENKO KK), 16 March 1989 * abstract *	1-6,8,22	B24D3/34 B24D11/02 C09K3/14
A	US 4 543 106 A (PAREKH) 24 September 1985 * abstract *	10-14	
A	US 4 111 667 A (ADAMS) 5 September 1978 * column 1, line 32 - line 61 *	10-14	
A	US 5 081 051 A (MATTINGLY ET AL.) 14 January 1992 * column 2, line 42 - line 65 *	16,17	
A	EP 0 439 124 A (MICRON TECHNOLOGY INC) 31 July 1991 * column 3, line 25 - column 4, line 44 *	18-21	
A	US 4 954 141 A (TAKIYAMA ET AL.) 4 September 1990 * the whole document *	1-3	TECHNICAL FIELDS SEARCHED (Int.Cl.6) B24B B24D

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	19 October 1998	Garella, M

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

22 (New). An aqueous polishing composition for a copper-containing semiconductor substrate having a surface requiring polishing, said polishing composition comprising:

a sufficient amount of an oxidizer; and

a sufficient amount of a corrosion inhibitor;

wherein said polishing composition has a pH to protect said surface from detrimental etching and corrosion in the absence of abrasive action and with little or no dishing in the presence of abrasive action.

23 (New). A polishing composition according to Claim 22 wherein said oxidizer and said corrosion inhibitor are present in said sufficient amounts to provide a corrosion current density less than 20 $\mu A/cm^2$ to protect said surface from detrimental etching and corrosion in the absence of abrasive action and with little or no dishing in the presence of abrasive action.

24 (New). A polishing composition according to Claim 22 wherein said oxidizer is present at about 0.01% to 7% by weight of said composition..

25 (New). A polishing composition according to Claim 22 wherein said corrosion inhibitor is present at about 0.001% to about 4% by weight of said composition.

26 (New). A polishing composition according to Claim 22 wherein said oxidizer is potassium iodate.

27 (New). A polishing composition according to Claim 22 wherein said corrosion inhibitor is benzotriazole.

28 (New). A polishing composition according to Claim 22 wherein the pH of said composition in a range of about 2 to about 4.

29 (New). A polishing composition according to Claim 28 wherein the pH is maintained in said range by utilizing a buffer at a concentration of about 0.1M to about 1M.

30 (New). A polishing composition according to Claim 22 wherein the pH of said composition is in a range of about 9 to about 10.

31(New). A polishing composition according to Claim 30 wherein the pH of said composition is maintained in said range by utilizing a buffer at a concentration of about 0.1M to about 1M.